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(54) **Single reactor process for preparing acrylic acid from propylene having improved capacity**  
Verfahren mit verbesserter Kapazität zur Herstellung von Acrylsäure aus Propylen in einem einzigen Reaktor  
Procédé de capacité améliorée utilisant un seul réacteur pour la préparation de l'acide acrylique à partir du propylène

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(73) Proprietor: **ROHM AND HAAS COMPANY**  
**Philadelphia, Pennsylvania 19106-2399 (US)**

(72) Inventors:  
• **Elder, James Edward**  
**Houston, TX 77096 (US)**  
• **Lonzetta, Charles Michael**  
**Houston, TX 77059 (US)**  
• **Hale, Timothy Allen**  
**Houston, TX 77035 (US)**

- **Sornson, John Dempster**  
**Moorestown, New Jersey 08057 (US)**
- **Klugherz, Peter David**  
**Huntingdon Valley, PA 19006 (US)**
- **Kaminski, Thomas Albert**  
**Houston, TX 77090 (US)**
- **Ebert, Donald Alan**  
**Houston, TX 77062 (US)**

(74) Representative: **Buckley, Guy Julian et al**  
**ROHM AND HAAS (UK) LTD.**  
**European Operations Patent Department**  
**Lennig House**  
**2 Mason's Avenue**  
**Croydon CR9 3NB (GB)**

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## Description

[0001] This invention relates to an improved process for preparing acrylic acid from propylene using a single reactor. In particular, the invention relates to a single reactor process for preparing acrylic acid from propylene utilizing an increased concentration of propylene reactant thereby providing increased capacity and throughput.

[0002] The preparation of acrylic acid from propylene generally proceeds in a vapor phase two step catalytic oxidation reaction. In the first step propylene is oxidized in the presence of oxygen, diluent inert gasses, water vapor, and appropriate catalysts to produce acrolein according to equation (I):



The acrolein is then oxidized, in a second step, in the presence of oxygen, diluent inert gasses, water vapor, and appropriate catalysts to form acrylic acid according to equation (II):



[0003] The two stage vapor phase catalytic oxidation of propylene to acrylic acid is generally performed using either tandem reactors wherein a separate reactor is utilized for each step (e.g., see the description in U.S. Patent No. 4,873,368) or by utilizing one reactor to perform both steps (e.g., see the description in U.S. Patent No. 4,526,783).

[0004] The acrylic acid prepared using such a vapor phase catalytic oxidation reaction is present in a mixed product gas exiting the reactor. Generally, the mixed product gas is cooled and is contacted with an aqueous stream in an absorption tower, thereby providing an aqueous acrylic acid solution from which acrylic acid can be isolated and purified. The remainder of the product gasses, known as the absorber waste gas or absorber off-gas, is incinerated or undergoes waste treatment. Depending on the reactants feed gas composition, the absorber off-gas may contain inert gasses,  $\text{O}_2$ , water vapor,  $\text{CO}$ ,  $\text{CO}_2$ , unreacted propylene, unreacted acrolein and/or acrylic acid.

[0005] It is known in the art to recycle at least a portion of the absorber off-gas back to the reactor(s) to provide inert diluent gas and steam to the reactant composition. The propylene in the reactant composition must be diluted because at high propylene concentrations the reaction may proceed too quickly and become difficult to control. Recycle of the absorber off-gas provides the necessary diluent gasses and steam to the reactor feed to assure a suitable propylene concentration. In addition, recycling the absorber off-gas serves to reduce waste water generated by the process by reducing the amount of steam that is fed to the process. Furthermore, small amounts of unreacted propylene and acrolein contained in the off-gas are given another chance to react and thereby improve the overall acrylic acid yield by optimizing conversions of propylene and acrolein.

[0006] When absorber off-gas recycle is not used, steam and nitrogen are used as the primary diluents. Steam is not consumed, but may alter the selectivity, conversion and/or catalytic activity in the oxidation reactions and is part of the mixed product gasses emerging from the reactor. When the mixed product gasses are introduced into the absorption column, the steam substantially condenses at the bottom of the absorption column and is a small part of the gasses flowing through the absorber.

[0007] However, a problem arises with absorber off-gas recycle. In contrast to the situation wherein absorber off-gas recycle is not used, a load develops at the top of the absorber because of the increased volume of inert gas flowing through the absorber. When absorber off-gas recycle is utilized, the off-gas is predominantly an inert gas such as nitrogen. When mixed product gasses containing such inert gasses are introduced into the absorber they do not generally condense at the absorber bottom, but rather remain part of the product gasses flowing through the absorber. Consequently, the increased inert gas content in the mixed product gasses introduced into the absorber causes an increase in the velocity of the gas flowing through the absorber. This results in a load at the top of the absorber. As the gas velocity gets higher, an increasing amount of product acrylic acid will remain with the absorber off-gas and be either lost to waste or be recycled back to the reactor. When it is recycled back to the reactor it can cause a decrease in catalyst activity. Consequently, regardless of whether it is lost to waste or recycles back to the reactor, the net result is a drop in acrylic acid yield.

[0008] A further problem results from the need to dilute the propylene in the gas feed to a manageable concentration. The dilution may be effected by absorber off-gas recycle or by adding steam and other inert materials or both. Because the two step oxidation of propylene to acrylic acid is highly exothermic, as the propylene concentration gets higher the danger of a runaway combustion increases. Also, the reaction mixture could become flammable and explode if ignited. Consequently, the oxidation of propylene to acrylic acid is generally practiced in the art utilizing a propylene concentration in the reactant gas feed composition of between 4 and 7 volume percent of the total reactant feed composition.

(see for example col. 2, lines 42-46 of U.S. patent No. 4,873,368). Accordingly, to assure control of the oxidation, propylene is diluted with steam and/or inert gases such as nitrogen and combined with oxygen to form the feed composition. As a result, there is an additional load on the compressor which limits the capacity of the system. Consequently, any increase in capacity would require a larger compressor to handle the larger load.

**[0009]** As a result of the extra load on the absorber and on the compressor there is a limit on the capacity of the system which heretofore could not be remedied except by installation of larger equipment.

**[0010]** A further problem exists when tandem reactors are utilized. In tandem reactors there exists a high volume interstage between the two reactors through which the acrolein produced in the first reactor passes to the second reactor. This results in a longer residence time, compared to a single reactor, of the acrolein product in the interstage which may lead to homogeneous reactions of acrolein and/or formation of foulants. Foulants may be formed by, for example, corrosion and deposition processes. Such homogeneous reactions are generally not catalytic, but rather are free radical reactions of acrolein which produce carbon oxides such as carbon dioxide and carbon monoxide, as well as other products such as acetaldehyde. Consequently, because of the longer interstage residence time in a tandem reactor process, steps such as cooling, reaction quenching, and acrolein dilution must be taken to reduce such homogeneous reactions of acrolein. In addition, the equipment and piping of the interstage is susceptible to gas leaks.

**[0011]** U.S. Patent Nos. 4,365,087 and 4,873,368 have dealt with the problem of increasing process productivity/capacity by raising the propylene concentration level. However, the processes in these references used a tandem reactor process whereby either the temperature of the feed was limited ( $< 260^{\circ}\text{C}$ ), the oxygen to propylene ratio (1.1 - 2.0 : 1, preferably lower than 1.8) was kept low, additional oxygen and inert gas was fed to the second stage reactor, and the reaction was quenched somewhat before introduction to the second stage ('087) or the oxygen to propylene ratio (1.17 - 1.66 : 1) was even lower, additional oxygen and inert gas was fed to the second stage reactor, and the reaction was quenched somewhat before introduction to the second stage. Accordingly, the basis of the technique relied on two mechanisms for controlling the reaction at higher propylene concentrations:

- (1) tightly controlling the temperature before entry into the first stage reactor and/or the second stage reactor; and
- (2) limiting the amount of oxygen initially available to the first reactor for oxidation of propylene to acrolein and then adding more oxygen and diluent at the interstage before the second stage reactor so that the second reactor feed has a stoichiometrically sufficient amount of oxygen to allow suitable oxidation of acrolein to acrylic acid.

**[0012]** However, this technique is unavailable for a single reactor system because it is implausible to add further oxygen and inert gas and quench the reaction at the interstage because both reactions of equations (I) and (II) occur in each of the reactor tubes of the single reactor.

**[0013]** U.S. patents 4,256,783 and 4,203,906 describe a single reactor system which is useful in a variety of catalytic vapor phase oxidation reactions including the preparation of acrolein and/or acrylic acid. However, the example relating to acrylic acid (see columns 9 and 10, Example 5 of the '783 patent) does not utilize a reactant feed having a higher propylene concentration.

**[0014]** The present inventors have now discovered that with the single reactor system described herein it is possible to provide feeds to the reactor which contain a higher concentration of propylene than previously thought. Such higher concentration feeds are accomplished without the need to utilize a lower oxygen:propylene feed ratio, quenching of the reaction between stages and the consequent addition of oxygen and inert gas to the second stage to assure proper stoichiometry. Consequently, less absorber off-gas is required for dilution so that loads on the absorber and compressor are lightened resulting in an increase in capacity without additional capital expenditure.

**[0015]** Furthermore, a process is provided wherein homogeneous reactions of acrolein, as well as other interstage reactions, and interstage gas leaks are substantially eliminated.

**[0016]** Accordingly, a novel process for preparing acrylic acid from propylene is described herein wherein the following advantages are provided:

- (1) increased throughput/capacity is provided without additional capital expenditure;
- (2) downstream debottlenecking is realized through producing an aqueous acrylic acid stream in the absorber having a higher concentration of acrylic acid because less water is condensed and less acrylic acid is lost overhead in the absorber;
- (3) since there is less water condensed in the aqueous acrylic acid there is a reduction in the waste generated by the process;
- (4) less system energy is required because of the reduced compressor load;
- (5) there is a lower pressure drop in the reactor, due to increased feed composition, which offsets increased propylene partial pressure, thereby preventing lower acrylic acid selectivity resulting from higher propylene pressure; and
- (6) interstage problems are substantially eliminated.

[0017] In one aspect of the present invention, there is provided a process for the vapor phase oxidation of propylene to acrylic acid, comprising the steps of: (A) feeding a reactant composition comprising: (i) at least 7.6 percent by volume propylene, (ii) oxygen, (iii) water vapor, and (iv) the remainder including a major amount of at least one inert gas, into a reactor; the reactor including a plurality of contact tubes, containing at least one catalyst, disposed in a shell, wherein the inside of the reactor shell is divided into at least first and second heat transfer zones through each of which a heat transfer medium passes and each contact tube comprises two or more reaction zones capable of effecting the preparation of acrylic acid from propylene, and (B) contacting the reactant composition with the two or more reaction zones to form a mixed product gas comprising acrylic acid.

[0018] In a second aspect of the present invention, there is provided a process for the vapor phase oxidation of propylene to acrylic acid, comprising the steps of: (A) feeding a reactant composition comprising: (i) at least 7.6 percent by volume propylene (ii) oxygen, (iii), water vapor and (iv) the remainder being a major amount of at least one inert gas and a minor amount of at least one inert gas suitable for use as a fuel, into a reactor; the reactor including a plurality of contact tubes, containing at least one catalyst, disposed in a shell, wherein the inside of the reactor shell is divided into first and second heat transfer zones through each of which a heat transfer medium passes, wherein each contact tube comprises two or more reaction zones capable of effecting the preparation of acrylic acid from propylene, and (B) contacting the reactant composition with the two or more reaction zones to form a mixed product gas comprising acrylic acid.

[0019] In a third aspect of the present invention, there is provided a process for the vapor phase oxidation of propylene to acrylic acid, comprising the steps of: (A) feeding a reactant composition comprising: (i) at least 7.6 percent by volume propylene, (ii) oxygen, (iii) water vapor, and (iv) the remainder being a major amount of at least one inert gas, into a reactor; the reactor including a plurality of contact tubes, containing at least one catalyst, disposed in a shell, wherein the inside of the reactor shell is divided into first and second heat transfer zones through each of which a heat transfer medium passes cocurrent to the reactant composition flow, wherein each contact tube comprises reaction zones A and A' which contain one or more catalysts capable of catalyzing oxidation of propylene to acrolein, reaction zones B and B' which contain one or more catalysts capable of catalyzing oxidation of acrolein to acrylic acid and a reaction zone C, containing a high surface area material having heat transfer properties and no percent catalyst, disposed between reaction zones A' and B, wherein the reaction zones A and A' have a different catalytic activity for converting propylene to acrolein and reaction zones B and B' have a different catalytic activity for converting acrolein to acrylic acid, and (B) contacting the reactant composition with the two or more reaction zones to form a mixed product gas comprising acrylic acid.

[0020] In a fourth aspect of the present invention, there is provided the use of a reactant feed composition in a process for vapor phase oxidation of propylene to acrylic acid in a single reactor, the composition including: (i) 7.6 to 11 percent by volume propylene, (ii) oxygen in an amount suitable to provide an oxygen to propylene ratio of 1.6 to 2.2:1.0, (iii) 2 to 12 percent by volume water vapor, and (iv) the remainder comprising a major amount of at least one inert gas selected from the group consisting of nitrogen, helium, argon and mixtures thereof, and a minor amount of at least one inert gas fuel.

[0021] Figure 1 depicts a flow chart showing one embodiment of the process of the present invention.

[0022] Figure 2 depicts one embodiment of a reactor useful in the process of the present invention.

[0023] Figure 3 depicts one embodiment of a catalytic contact tube of a reactor useful in the process of the present invention.

[0024] Throughout this specification and claims, unless otherwise indicated, references to percentages are by molar volume and all temperatures are in degree centigrade.

[0025] It is also to be understood that for purposes of this specification and claims that the range and ratio limits, recited herein, are combinable. For example, if ranges of 1-20 and 5-15 are recited for a particular parameter, it is understood that ranges of 1-15 or 5-20 are also contemplated.

[0026] Throughout this specification and claims the terms "water vapor" and "steam" are understood to be synonymous.

[0027] Also, the term "major amount" is understood to mean greater than 50 percent by volume of the total composition. The term "minor amount" is understood to mean less than 50 percent by volume of the total composition.

[0028] The term "cocurrent" as used herein is meant to indicate that the current of separate, distinct flowing materials is proceeding in substantially the same general direction, regardless of any alterations such as meandering, transverse, or radial flow.

[0029] The term "countercurrent" as used herein is meant to indicate that the current of separate, distinct flowing materials is proceeding in substantially the opposite general direction, regardless of any alterations such as meandering, transverse, or radial flow.

[0030] The term "inert" as used herein is meant to indicate that the particular material does not participate in, is unaffected by, and/or is otherwise inactive in the acrylic acid reaction system disclosed herein. Accordingly, a material such as propane is easily reacted or combusted in other systems, but in the reaction system of the present invention

is considered in it.

[0031] The term "catalyst" as used herein refers to pure catalysts, or pure catalyst provided on a support, by coating, impregnating etc., such pure catalyst on a support material. Accordingly, the terminology 100 percent catalyst refers not only to a material which is pure catalyst, but to 100 percent of a material which includes catalyst on a support material and/or impurities when purchased. That is, 100 percent catalyst refers to 100 percent of the catalyst as purchased, whether it be as neat chemical or with a support material.

The conversion % of propylene = (# moles propylene converted / # of moles  
propylene employed) x 100.

The selectivity % of acrylic acid = (# of moles of acrylic acid produced / #  
of moles propylene reacted) x 100.

The yield of acrylic acid = (# of moles acrylic acid produced / # of moles  
propylene employed) x 100.

The yield of acrolein = (# of moles acrolein produced / # of moles propylene  
employed) x 100.

[0032] As recited above, the process for preparing acrylic acid from propylene includes feeding a reactant composition into a reactor. The reactant composition includes propylene, oxygen, water vapor, and inert gas.

[0033] The propylene used may be from any source and may be any grade suitable for an acrylic acid producing vapor phase oxidation reaction. Suitable grades include, but are not limited to, polymer grade (generally greater than or equal to 99% propylene), chemical grade (generally greater than or equal to 94% propylene), and refinery grade (generally greater than or equal to 60% propylene). In a preferred embodiment, the propylene is chemical grade propylene. Use of chemical grade propylene has the added advantage of providing combustible materials such as propane which are present as impurities. The propane provides more inert gas to the system, but more importantly provides fuel for the thermal/catalytic oxidation or incineration of that portion of the absorber off-gas which is not recycled. Accordingly, the propane impurity enters the thermal/catalytic oxidizer or incinerator with the absorber off-gas and reduces the additional fuel required to burn the off-gas. Generally, chemical grade propylene contains up to 6 percent combustible impurities and refinery grade propylene contains up to 40 percent combustible impurities.

[0034] Propylene is generally present in the reactant composition in at least 7.6 percent by volume of the reactant composition. In one embodiment, propylene is present at a range of from 7.6 to 11, preferably, 7.6 to 9 percent by volume of the reactant composition.

[0035] The oxygen in the reaction composition may be provided by any material containing an amount of oxygen sufficient to maintain the oxidation reactions in equations (I) and (II) above. Suitable examples include, without limitation, air, oxygen-enriched air, pure oxygen, and mixtures of pure oxygen and at least one inert gas or mixtures thereof. The preferred source of oxygen is air. Typically oxygen is present in the reactant composition in an amount suitable to meet the stoichiometric needs of the reaction. Generally, an amount of oxygen which will provide an oxygen/propylene ratio in the reactant composition of 1.6 to 2.2: 1.0, preferably 1.6 to 2.0: 1.0, is provided.

[0036] The water vapor in the reaction composition is generally present at a range from 2 to 12, preferably 5 to 11 percent by volume of the reactant composition. The water vapor may be provided by absorber off-gas recycle, or be otherwise generated and provided to the reactant composition or may be provided by both absorber off-gas recycle and generation.

[0037] The inert gas used in the reaction composition may be any gaseous material or mixtures of gaseous materials which is inert to the oxidation reactions depicted in equations (I) and (II) above. Typical examples include, but are not limited to, nitrogen, carbon dioxide, helium, argon, propane and carbon monoxide, or mixtures thereof. The preferred inert gas is nitrogen or a mixture of nitrogen with at least one other inert gas. The inert gas generally constitutes a major amount of the remainder of the reactant composition which is not propylene, oxygen, or water vapor. Generally, the inert gas is 50 to 99.9, preferably 60 to 99.9 volume percent of the remainder of the reactant composition.

[0038] As recited above, the reaction composition may optionally include at least one inert gas which is suitable for use as fuel for thermal oxidation/incineration of waste absorber off-gas. Such inert gas fuel may be provided as part of the impurities in the propylene feed, as part of the absorber off-gas, or as the neat chemical. Suitable examples include, but are not limited to, propane, ethane, methane, butane, pentane or mixtures of one or more of the above. The preferred inert gas fuel is propane. Generally, such inert gas fuel is present in a minor amount in the remainder of the reactant composition which does not include propylene, oxygen and water vapor. Generally, the inert gas fuel is 0.001 to 49.9, preferably 0.1 to 20 volume percent of the remainder of the reactant composition.

[0039] In a preferred embodiment, the water vapor and inert gas and optionally at least a portion of the inert gas fuel, of the reaction composition, are provided by recycle of the absorber off-gas to the reactor. Generally, an amount of absorber off-gas is recycled which is suitable to provide the appropriate amounts of water vapor and inert gas. However, it is understood by those skilled in the art that the absorber off-gas may not provide all of the requirements of water vapor and/or inert gas of the system and additional amounts may be added from other sources. The water vapor and inert gas from the absorber off-gas are combined with oxygen and propylene as shown in Figure 1. Air is heated in inlet air heater 1 and is combined with recycle gas from the top of absorber 2 which has been reheated in the absorber off-gas reheater 3 in the suction 4 of the compressor 5. (The gasses are heated before mixing and feeding to the compressor to prevent fogging and/or condensation which might damage the compressor.) This mixture is pumped to the feed gas mixer 6 by the compressor 5 where the air and absorber off-gas mixture is combined with propylene and any additional steam required. The reactant composition is then fed to the reactor 7 at reactor inlet 29 into the contact tubes 9. The product gasses emerge from outlet 30.

[0040] The reactor 7 is a shell and multiple contact tube heat exchange reactor. As depicted in Figure 2, the reactor 7 includes a plurality of catalytic contact tubes 9 disposed in a shell 8 and passed through a perforated tube sheet 10 which divides the inside of the reactor shell into first heat transfer zone 11 and a second heat transfer zone 12 through each of which a heat transfer medium passes. The contact tubes 9 run longitudinally from the top portion to the bottom portion of the reactor 7 through the perforated tubesheet 10. It is understood that the reactor 7 may contain one or more perforated tubesheets which divide the reactor into two or more heat transfer zones.

[0041] Each of the plurality of contact tubes 9 includes two or more reaction zones which individually or in combination are capable of effecting the preparation of acrylic acid from propylene. At least one of the reaction zones contains a catalyst mixture capable of effecting the preparation of acrylic acid from propylene. In one embodiment, each of the contact tubes 9 contains a reaction zone A containing catalyst at least capable of catalyzing oxidation of propylene to acrolein and a reaction zone B containing catalyst at least capable of catalyzing oxidation of acrolein to acrylic acid. The reaction zones A and B may overlap or be intertwined or be disposed within the contact tubes 9 sequentially so that the reactants contact reaction zone A first and then reaction zone B.

[0042] In an alternative embodiment, each of the plurality of contact tubes 9 include reaction zones A and A' which contain one or more catalysts at least capable of catalyzing oxidation of propylene to acrolein and reaction zones B and B' which contain one or more catalysts at least capable of catalyzing oxidation of acrolein to acrylic acid. In one embodiment, reaction zones A and A' have a different catalytic activity for converting propylene into acrolein and/or reaction zones B and B' have a different activity for converting acrolein to acrylic acid.

[0043] In another embodiment, the two previous embodiments may be combined so that each contact tube 9 may have reaction zones A, A' and B; A, A', and B'; A, B, and B'; or A', B, and B'.

[0044] In a further embodiment, a reaction zone C containing 0 percent by weight catalyst is disposed between A type reaction zones (e.g., A or A' etc.) and B type reaction zones (e.g., B or B' etc.) in each contact tube 9. Generally, zone C is less than 10 percent of the total length of the contact tube. For instance in one embodiment zone C is 350 to 850, preferably 380 to 650 mm long. In a preferred embodiment, the reaction zone C is packed with a high surface area material with a heat transfer enhancing shape which is inert to and stable in the reaction system. Suitable examples include, alumina, alundum, mullite, carborundum, steel including stainless steel, copper, aluminum and ceramics. Furthermore, as stated above the material should be in a form in which its outer surface area is large including, without limitation, small spheres, cylinders, rings, small pieces, filament, meshes and ribbons.

[0045] Because of the short length of the reaction zone C, the reaction gasses have a short residence time in this zone of the contact tubes. As a result of this short residence time, the problems recited above which are inherent in a tandem reactor system do not occur in the process of the present invention. This is because gas wall molecular collisions occurring in zone C are enhanced by high surface area packing materials. Such molecular collisions tend to reduce the free radical homogenous reactions of acrolein by dissipating the kinetic energy of the system and therefore reduce free radical formation.

[0046] A preferred embodiment of a catalytic contact tube 9 of the present invention is shown in Figure 3. The reaction gasses flow into reaction zone A at the bottom of the reactor. The first layer 13 in the bottom of contact tube 9 is a diluent material which is primarily ceramic balls or cylinders. Suitable ceramic materials as well as other type materials include, without limitation, one or more of the following: silicon dioxide, silicon carbide, silicon nitride, silicon boride, silicon boronitride, aluminum oxide (alumina), aluminosilicate (mullite), alundum, aluminoborosilicate, carborundum,

carbon-fiber, refractory fiber, zirconium oxid , yttrium oxid , calcium oxid , magnesium oxid , magnesium oxide-aluminosilicate (cordite), and clay based materials. Suitable diluent materials are available, for instance, from Norton Chemical Process Products Corp., of Akron, Ohio as the Denstone® line of catalyst supports. As it passes the diluent material the reactant composition is preheated to near the temperature of the heat transfer medium before it enters reaction zone A 14. Reaction zone A 14 is a mixture of a catalyst capable of catalyzing the oxidation of propylene to acrolein and a diluent material. The mixture of catalyst and diluent material is less active than pure catalyst, thus making the reaction cooler and easier to control at the high initial propylene concentration. Determination of the amount of dilution of the catalyst is within the skill of those skilled in the art and generally is dependent on, for example, the particular catalyst utilized as well as the age of the catalyst and the operating conditions of the process. As the gas flows up the tube, the temperature increases as the reaction rate increases, then cools down as the propylene concentration decreases.

[0047] From reaction zone A 14 the reaction gasses flow into reaction zone A' 15 which has a higher catalytic activity than zone A 14. As a result, the reaction rate increases again and then decreases with declining propylene concentration. Zone A' 15 is longer than zone A 14, generally at least 50 % longer, because more exposure to the higher activity catalyst is needed to convert substantially all of the propylene to acrolein which is being generated in situ in reaction zones A 14 and A' 15 along with some acrylic acid. Preferably, the ratio of the length of A'/A is 1.0:1 to 3.0:1, more preferably 1.5:1 to 2.5:1.

[0048] After traversing reaction zones A 14 and A' 15 the reaction gasses enter reaction zone C 16 which contains no catalyst but rather is packed with stainless steel Raschig rings or other suitable heat transfer material which have good heat transfer properties and increase the surface area of zone C. Reaction zone C 16 begins in the first heat transfer zone 11 and extends past the perforated tubesheet 10 into the second heat transfer zone 12. Reaction zone C 16 provides a short time for cooling the reaction gas to help control the oxidation reactions.

[0049] After passing reaction zone C 16 the reaction gasses enter reaction zone B 17. Reaction zone B 17 is a mixture of a catalyst capable of catalyzing the oxidation of acrolein to acrylic acid and a diluent material. As described for reaction zone A 14, the mixture of catalyst and diluent material is less active than pure catalyst, thus making the reaction cooler and easier to control at the high initial acrolein concentration generated in situ in zones A 14 and A' 15. Also, as described above, determination of the amount of dilution of the catalyst is within the skill of those skilled in the art and generally is dependent on, for example, the particular catalyst utilized as well as the age of the catalyst and the operating conditions of the process. As the gas flows up the tube the temperature increases as the reaction rate increases, then cools down as the acrolein concentration decreases.

[0050] From reaction zone B 17 the reaction gasses flow into reaction zone B' 18 which has a higher catalytic activity than zone B 17. As a result, the reaction rate increases again and then decreases with declining acrolein concentration. Zone B' 18 is longer than zone B 17, generally at least 50% longer, because more exposure to the higher activity catalyst is needed to maximize conversion of the acrolein to acrylic acid. Preferably, the ratio of the length of B'/B is 1.0:1 to 3.0:1, more preferably 1.5:1 to 2.5:1.

[0051] The mixed product gas containing acrylic acid then flows out of the contact tubes 9 of the reactor 7 through a layer of inert material which is larger than the catalyst. The inert material holds catalyst within the contact tubes 9. Normal gas flows will not blow catalyst out of the tubes, but abnormal conditions might result in high gas velocities that could.

[0052] In one embodiment, the reactor 7 contains greater than 15,000 contact tubes 9. In a preferred embodiment, the reactor 7 contains greater than 25,000 contact tubes 9. The contact tubes 9 utilized are those generally known and used in the art. The contact tubes 9 may be arranged in any suitable arrangement known in the art. Such suitable arrangements are described and disclosed in, for instance, U.S. Patent Nos. 4,256,783; 5,151,605; and DE 2,201,528.

[0053] Any catalysts suitable for the vapor phase catalytic oxidation of propylene to acrolein and acrolein to acrylic acid may be used in the process of the present invention. Such catalysts are known in the art and are described in, for instance U.S. Patent Nos. 3,775,474; 3,893,951; 3,954,855; 4,075,127; 4,365,087; 4,873,368; 5,144,091; 5,177,260; 5,198,578; 5,264,625; 5,739,391; 5,739,392; WIPO Patent App. No. WO 97/36849; and Canadian Patent App. No. 2,114,681.

[0054] As recited above, the reactor 7 is divided into a first heat transfer zone 11 and a second heat transfer zone 12 by a perforated tubesheet 10 through which the contact tubes 9 pass. The first heat transfer zone 11 generally corresponds to that portion of the reactor 7 where the oxidation of propylene to acrolein predominantly occurs in the contact tubes 9. In a like manner, the second heat transfer zone 12, corresponds to that portion of the reactor 7 where oxidation of acrolein to acrylic acid predominantly occurs in the contact tubes 9. It is also recognized that some oxidation to acrylic acid may occur in reaction zones A and A' and oxidation of propylene to acrolein may occur in reaction zones B and B'. Accordingly, the contact tubes 9 are arranged so that the appropriate reaction zones are positioned in the appropriate heat transfer zone.

[0055] Each heat transfer zone has circulating within it a heat transfer medium which is used to maintain an effective catalyst temperature profile and therefore reaction temperature. Maintaining a desired catalyst temperature profile is

required for maintaining the optimum acrylic acid yield and for optimizing catalyst life. If the reaction temperature is too high, more carbon dioxide and carbon monoxide are formed thereby resulting in lower yields. Furthermore, the catalyst will age quicker under excessive reaction temperatures. Of course, if the temperature gets high enough an uncontrolled runaway reaction may occur. If not controlled, such a reaction could lead to catalyst destruction and/or explosive conditions. If the reaction temperature is too low, less propylene will be converted to acrolein and acrolein to acrylic acid so that yields will be lower. If the reaction temperature is excessively low, propylene and/or acrolein may travel downstream leading to serious consequences.

[0056] The heat transfer medium circulates within each heat transfer zone thereby transferring heat from those outer portions of the contact tubes it contacts in the particular zone. The first heat transfer zone 11 is maintained at a temperature of 250 to 450, preferably 280 to 380°C; and the second heat transfer zone 12 is maintained at a temperature of 220 to 450, preferably 240 to 360°C. The peak catalyst temperatures are 20 to 70°C above the heat transfer medium temperature and are very sensitive to changes in the heat transfer medium temperature. Generally, increasing the heat transfer medium temperature by 1 °C will increase the peak catalyst temperature by 2-3°C. As is known in the art the catalyst will lose activity as it grows older. To compensate, reaction temperature must be increased to maintain production of acrolein and acrylic acid at desired levels.

[0057] The heat transfer medium may circulate in any manner deemed suitable for the particular reactor system utilized. In one embodiment, the heat transfer medium circulates within the reactor cocurrent with the flow of the reactant gasses through the reactor. It is understood that the cocurrent flow may proceed top to bottom, bottom to top or side to side in the reactor 7. In an alternative embodiment, the heat transfer medium circulates within the reactor countercurrent with the flow of the reactant gasses through the reactor. In a preferred embodiment, the heat transfer medium circulates within the reactor both cocurrent with the flow of the reactant gasses and transverse both away from and towards the center of the reactor in a meandering flow. In a further preferred embodiment, a bypass flow of the heat transfer medium is provided. U.S. Patent Nos. 4,256,783; 5,151,605; 5,739,391; and DE 2,201,528, describe and disclose contact tube and baffle arrangements in contact tube fixed bed shell reactors which provide for cocurrent, countercurrent, transverse and bypass flows of the heat transfer medium, such references being incorporated herein by reference for their teaching of heat transfer medium flow and reactor arrangements to accomplish the same. Furthermore, it is understood that the baffles may be arranged so as to have equal spacing between baffles or variable spacing between baffles.

[0058] The heat transfer medium may be any heat transfer medium suitable for use under the temperature conditions of the present invention. Generally the heat transfer medium is a salt melt, preferably a salt melt of 40 to 80, preferably 50 to 70 percent by weight potassium nitrate and 60 to 20, preferably 50 to 30 percent by weight sodium nitrite. In an alternative embodiment, the salt melt may include sodium nitrate as a substitute for sodium nitrite or potassium nitrate or as an additional component of the salt melt. The sodium nitrate is generally present at up to 20, preferably up to 10 percent by weight of the total salt composition. Other examples of heat transfer mediums include heat transfer oils, both oleaginous and synthetic, heat transfer fluids such as phenyl ethers and polyphenyls, and low melting metals such as sodium, tin, mercury, as well as low melting alloys of various metals.

[0059] In one embodiment, the heat transfer medium circulates within the reactor in at least two distinct heat transfer medium circuits. Preferably, at least one circuit is in each heat transfer zone. The heat transfer circuit is described as follows. The heat transfer medium enters the reactor shell at a plurality of points. In a preferred embodiment, the heat transfer medium flows into a channel 20a and 20b which completely circles the reactor 7. The heat transfer medium then flows from the channel 20a and 20b into the reactor 7 through windows in the shell of the reactor. Accordingly, the heat transfer medium flows into the reactor 7 around the reactor's entire perimeter. The heat transfer medium flows around the contact tubes and is forced into the center of the reactor by a doughnut baffle 21 which is a steel plate with a large hole in the center. The heat transfer medium flows through the hole and is forced back toward the perimeter of the reactor by a disk baffle 22 which is a large round plate which stops short of the reactor shell. The heat transfer medium flows through a series of the doughnut and disk baffles establishing a cocurrent/transverse flow of the heat transfer medium with the reactant gasses flow. After flowing through the baffles the heat transfer medium exits through windows through exit channels 21a and 21b, similar to the entry channel, back to heat transfer medium pumps for recirculation.

[0060] In an alternative embodiment, the heat transfer circuit contains a cooling circuit whereby a portion of the heat transfer medium of each heat transfer medium circuit is circulated to the outside of the reactor for cooling and then returned to the heat transfer medium circuit. In a further preferred embodiment, the heat transfer medium circulates within the reactor in at least two distinct heat transfer medium circuits at least one of which is a bypass circuit where at least a portion of the heat transfer medium circulates in a manner so as to bypass contact with at least a portion of the contact tubes 9. In an alternative preferred embodiment, the at least two distinct heat transfer medium circuits include two distinct heat transfer medium circuits as well as both a cooling circuit and a bypass circuit.

[0061] The process of the present invention optionally includes a step (C) contacting the mixed product gasses with an aqueous stream in an absorption tower 2 to obtain an aqueous acrylic acid solution. Generally, hot mixed product



gasses exit the reactor and flow into the bottom section of the absorber wherein it is quenched by contact with a circulating absorber bottoms stream 23. A portion of the product acrylic acid is absorbed here while most of the remainder is absorbed in the upper section where the gas is contacted with an aqueous stream 24 fed into the top of the absorber. Any acrylic acid remaining in the absorber off-gas stream is sent to the incinerator 26 or recycled 27 to the reactor. Some of the reaction by-products, including acetic acid, formaldehyde, maleic acid and other organics, are absorbed along with the acrylic acid. Unreacted propylene, most of the unreacted acrolein, inert fuel gas such as propane, CO<sub>2</sub>, O<sub>2</sub>, CO, and N<sub>2</sub> are not absorbed and leave the absorber 2 as the absorber off-gas. Also part of the absorber off-gas is acrylic acid as well as other byproducts of the reaction which have not been absorbed. The absorber off-gas is sent to the thermal/catalytic oxidizer or incinerator or are recycled to the reactor as described above.

[0062] The aqueous stream 24 may be an essentially pure water stream, e.g., deionized water, a recycled aqueous wastewater stream or a mixture thereof. Typically, if a waste water stream is utilized the stream will contain a major amount of water and minor amounts of acrylic acid, acetic acid, distillation solvent(s), or mixtures of one or more thereof. In one embodiment, the recycled wastewater stream contains less than 3.0, preferably 0.001 to 2.5, more preferably 0.001 to 1.5 percent by weight acetic acid.

[0063] In a further embodiment, the aqueous stream 24 includes a polymerization inhibitor. The polymerization inhibitor may include a water soluble or alcohol soluble polymerization inhibitor. Suitable examples include but are not limited to, hydroquinone; 4-methoxyphenol; 4-ethoxyphenol; 4-propoxyphenol; 4-butoxyphenol; 4-heptoxyphenol; hydroquinone monobenzylether; 1,2-dihydroxybenzene; 2-methoxyphenol; 2,5-dichlorhydroquinone; 2,5-di-tert-butylhydroquinone; 2-acetylhydroquinone; hydroquinone monobenzoate; 1,4-dimercaptobenzene; 1,2-dimercaptobenzene; 2,3,5-trimethylhydroquinone; 4-aminophenol; 2-aminophenol; 2-N, N-dimethylaminophenol; 2-mercaptophenol; 4-mercaptophenol; catechol; monobutylether; 4-ethylaminophenol; 2,3-dihydroxyacetophenone; pyrogallol; 1,2-dimethylether; 2-methylthiophenol; t-butyl catechol; di-tert-butyl nitroxide; di-tert-amyl nitroxide; 2,2,6,6-tetramethyl-piperidinyloxy; 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy; 4-oxo-2,2,6,6-tetramethyl-piperidinyloxy; 4-dimethylamino-2,2,6,6-tetramethyl-piperidinyloxy; 4-amino-2,2,6,6-tetramethyl-piperidinyloxy; 4-ethanoyloxy-2,2,6,6-tetramethyl-piperidinyloxy; 2,2,5,5-tetramethyl-pyrrolidinyloxy; 3-amino-2,2,5,5-tetramethylpyrrolidinyloxy; 2,2,5,5-tetramethyl-1-oxa-3-azacyclopentyl-3-oxy; 2,2,5,5-tetramethyl-3-pyrrolinyl-1-oxy-3-carboxylic acid; 2,2,3,3,5,5,6,6-octamethyl-1,4-diazacyclohexyl-1,4-dioxy; copper compounds such as copper dimethyldithiocarbamate; copper diethyldithiocarbamate; copper salicylate; isomers thereof; mixtures of two or more thereof; or mixtures of one or more of the above with molecular oxygen. Preferably, the polymerization inhibitor is hydroquinone, 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy, mixtures thereof; or mixtures of one or more of the above with molecular oxygen; more preferably the polymerization inhibitor is hydroquinone.

[0064] At least a portion of the absorber off-gas leaving the top of the absorber is recycled to the reactor as described above. The remaining portion is sent to a thermal oxidizer or incinerator wherein the organics in the stream are burned/oxidized for pollution prevention.

[0065] The process of the present invention optionally includes a step (D) stripping light ends from the aqueous acrylic acid solution emanating from the absorber 2 in a light ends stripper 28. Typically, the aqueous acrylic acid effluent from the absorber 2 is pumped to the light ends stripper 28. In the light ends stripper 28, light ends, including acrolein, are stripped out of the aqueous acrylic acid stream. The overhead stream from the light ends stripper is mostly water and acrolein which is condensed and recycled 31 to the absorber. This has the effect of concentrating the light ends in the absorber and eventually forcing them out in the absorber off-gas. The stripped aqueous acrylic acid solution from the bottom of the light ends stripper is introduced into a separations unit 32 wherein the acrylic acid is isolated and purified to provide the desired grade of acrylic acid product. Generally, the concentration of acrylic acid in the stripped aqueous acrylic acid solution is 55 to 85, preferably 60 to 80 percent by weight.

[0066] The polymerization inhibitor introduced into the absorber generally remains in the aqueous-acrylic acid stream and inhibits polymerization of acrylic acid in the light ends stripping process. The following Examples are provided as an illustration of the present invention.

#### Comparative Example 1

[0067] A feed composition containing 6.9% by volume chemical grade propylene, an amount of air and absorber off-gas sufficient to maintain an oxygen/propylene ratio of 1.9 and 8.9% by volume water vapor were fed to the contact tubes of a reactor as described by Figures 2 and 3. The reactants were introduced into the contact tubes which were packed with ACF-4 catalyst (zones A and A') and ACS-6 catalyst (zones B and B'), both available from Nippon Shokubai K.K. of Osaka, Japan, as described in Figure 3. Zones A and B were diluted with inert Denstone 57 catalyst bed supports available from Norton Chemical Products Corp., of Akron, Ohio so that zone A was 66% catalyst and zone B was 87% catalyst where the ratio of the length of zones A/A' and B/B' are both 1/2. Zones A' and B' contained 100% of the ACF-4 and ACS-6 catalysts respectively. The acrylic acid formation reactions were carried out at a salt temperature maintained at 310 to 320°C in Zone A and 300 to 310 °C in Zone B for a trial time of 12966 hours. The

product gasses containing acrylic acid were introduced into an absorption tower to obtain an aqueous acrylic acid product solution. The aqueous acrylic acid solution was stripped of light ends in a light ends stripper to obtain an aqueous acrylic acid stream having an average concentration of 65.2 weight %.

#### 5 Example 1

[0068] This example was run according to the procedure of Comparative Example 1 except that the feed composition contained 7.6% by volume chemical grade propylene, an amount of air and absorber off-gas sufficient to maintain an oxygen/propylene ratio of 1.8 and 8.5% by volume water vapor and the Zone B salt temperature was maintained at 280 to 290°C in Zone B. The Zone B salt temperature was different because the Zone B catalyst in the comparative example was a different age from that used in this example thereby requiring an adjustment in temperature to maintain the same catalytic activity. The trial time was 12545 hours. An aqueous acrylic acid stream having an average concentration of 69.5 weight % was obtained.

#### 15 Example 2

[0069] This example was run according to the procedure of Comparative Example 1 except that the feed composition contained 8.1% by volume chemical grade propylene, an amount of air and absorber off-gas sufficient to maintain an oxygen/propylene ratio of 1.8 and 7.6% by volume water vapor and the Zone B salt temperature was maintained at 280 to 290 °C in Zone B. The Zone B salt temperature was different because the Zone B catalyst in the comparative example was a different age than that used in this example thereby requiring an adjustment in temperature to maintain the same catalytic activity. The trial time was 23407 hours. An aqueous acrylic acid stream having an average concentration of 73.8 weight % was obtained.

[0070] The average overall propylene conversion, acrylic acid yield, and acrolein yield obtained for Comparative Example 1 and for Examples 1 and 2 remained substantially the same. The acrylic acid concentration in the aqueous stream emanating from the light ends stripper increased with increasing propylene percentage in the feed gasses. Accordingly, since the yield of acrylic acid remained substantially the same, the amount of acrylic acid produced per unit volume is increased. The ability to economically increase aqueous strength without excess acrylic acid losses in the absorber off-gas is illustrated by the general increase in acrylic acid concentration in the resulting aqueous stream. Generally, as the propylene partial pressure in the first stage of the reactor increases the acrylic acid yield decreases. This relationship is countered in the present invention by a decrease in reactor inlet pressure at higher propylene feed concentrations. The net result is that the overall AA yield is essentially constant as propylene concentrations are increased.

#### 35 Claims

1. A process for the vapor phase oxidation of propylene to acrylic acid, comprising the steps of:

(A) feeding a reactant composition comprising:

- (i) at least 7.6 percent by volume propylene,
- (ii) oxygen,
- (iii) water vapor, and
- (iv) the remainder comprising a major amount of inert gas,

into a reactor; the reactor including a plurality of contact tubes, containing at least one catalyst, disposed in a shell, wherein the inside of the reactor shell is divided into at least first and second heat transfer zones through each of which a heat transfer medium passes and each contact tube comprises two or more reaction zones capable of effecting the preparation of acrylic acid from propylene, wherein the heat transfer zones are formed by at least one perforated tube sheet through which the catalytic contact tubes pass; and

(B) contacting the reactant composition with the two or more reaction zones to form a mixed product gas comprising acrylic acid.

2. The process of claim 1, wherein the reactant composition contains 7.6 to 11 percent by volume propylene.

3. The process of claim 1, wherein the reactant composition oxygen is present in an amount which provides an oxygen/propylene ratio of 1.6 to 2.0: 1.0.

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4. The process of claim 1, wherein the reactant composition contains 2 to 12 percent by volume water vapor.
5. The process of claim 1, wherein the heat transfer zones are formed by at least one perforated tube sheet through which the catalytic contact tubes pass.
6. The process of claim 1, wherein the two or more reaction zones include a reaction zone A containing catalyst at least capable of catalyzing oxidation of propylene to acrolein and a reaction zone B containing catalyst at least capable of catalyzing oxidation of acrolein to acrylic acid.
7. The process of claim 6, wherein the two or more reaction zones may overlap.
8. The process of claim 6, wherein the reaction zones A and B are disposed within the reactor tubes sequentially so that the reactants contact reaction zone A first and then reaction zone B.
9. The process of claim 1, wherein the two or more reaction zones include reaction zones A and A' which contain one or more catalysts at least capable of catalyzing oxidation of propylene to acrolein and reaction zones B and B' which contain one or more catalysts at least capable of catalyzing oxidation of acrolein to acrylic acid.
10. The process of claim 9, wherein the reaction zones A and A' have a different catalytic activity for converting propylene to acrolein.
11. The process of claim 10, wherein reaction zones B and B' have a different catalytic activity for converting acrolein to acrylic acid.
12. The process of claim 6, wherein the contact tube further comprises a reaction zone containing 0 percent catalyst disposed between the first and second reaction zones.
13. The process of claim 9, wherein the contact tube further comprises a reaction zone containing 0 percent catalyst disposed between reaction zones A' and B.
14. The process of claim 1, wherein the reactor contains greater than 15,000 contact tubes.
15. The process of claim 9, wherein the ratios of A'/A and B'/B are both 1.0:1 to 3.0:1.
16. The process of claim 1, wherein the first heat transfer zone is maintained at a temperature of 250 to 450 °C.
17. The process of claim 1, wherein the second heat transfer zone is maintained at a temperature of 220 to 450 °C.
18. The process of claim 1, wherein the heat transfer medium circulates within the reactor cocurrent with the flow of the reactants.
19. The process of claim 1, wherein the heat transfer medium circulates within the reactor countercurrent with the flow of the reactants.
20. The process of claim 1, wherein the heat transfer medium circulates within the reactor in at least two distinct heat transfer medium circuits.
21. The process of claim 1, wherein the heat transfer medium enters the reactor through the shell at a plurality of entry points.
22. The process of claim 18, wherein the heat transfer medium circulates within the reactor both cocurrent with the reactants and transverse both away from and towards the center of the reactor in a meandering flow.
23. The process of claim 20, wherein at least one of the heat transfer medium circuits contains a cooling circuit whereby a portion of the heat transfer medium of the heat transfer medium circuit is circulated to the outside of the reactor for cooling and then returned to at least one of the heat transfer medium circuits.
24. The process of claim 20, wherein the heat transfer medium circulates within the reactor in at least two distinct heat

transfer medium circuits, at least one of which is a bypass circuit where at least a portion of the heat transfer medium circulates in a manner so as to bypass contact with at least a portion of the contact tubes.

25. The process of claim 1, further comprising step (C) contacting the mixed product gas with an aqueous stream in an absorption tower to obtain an aqueous acrylic acid solution.

26. The process of claim 25, wherein at least a portion of absorber off-gas produced during step (C) is combined with reactants to form the reactant composition.

27. The process of claim 26, wherein the portion of absorber off-gas provided is an amount suitable to maintain at least 7.6 percent by volume propylene in the reactant composition.

28. The process of claim 25, wherein the aqueous stream comprises water and at least one polymerization inhibitor.

29. The process of claim 28, wherein the at least one polymerization inhibitor is selected from a water soluble or alcohol soluble polymerization inhibitor.

30. The process of claim 28, wherein the at least one polymerization inhibitor is utilized in combination with oxygen.

31. The process of claim 25, wherein the aqueous stream comprises less than 3.0 percent by weight acetic acid.

32. The process of claim 31, wherein at least a portion of the aqueous stream is a recycled waste water stream.

33. The process of claim 25, further comprising step (D) stripping light ends from the aqueous acrylic acid solution emanating from the absorber.

34. A process for the vapor phase oxidation of propylene to acrylic acid as claimed in claim 1, comprising the steps of:

(A) feeding a reactant composition comprising:

- (i) at least 7.6 percent by volume propylene,
- (ii) oxygen,
- (iii) water vapor, and
- (iv) with the remainder being a major amount of at least one inert gas and a minor amount of at least one inert gas suitable for use as a fuel,

into a reactor; the reactor including a plurality of contact tubes containing at least one catalyst disposed in a shell, wherein the inside of the reactor shell is divided into first and second heat transfer zones through each of which a heat transfer medium passes, wherein each contact tube comprises two or more reaction zones capable of effecting the preparation of acrylic acid from propylene, wherein the heat transfer zones are formed by at least one perforated tube sheet through which the catalytic contact tubes pass; and  
(B) contacting the reactant composition with the two or more reaction zones to form a mixed product gas comprising acrylic acid.

35. A process for the vapor phase oxidation of propylene to acrylic acid as claimed in claim 1, comprising the steps of:

(A) feeding a reactant composition comprising:

- (i) at least 7.6 percent by volume propylene,
- (ii) oxygen,
- (iii) water vapor, and
- (iv) the remainder being a major amount of at least one inert gas,

into a reactor; the reactor including a plurality of contact tubes containing at least one catalyst disposed in a shell, wherein the inside of the shell is divided into first and second heat transfer zones through each of which a heat transfer medium passes cocurrent to the reactant composition flow, wherein each contact tube at least comprises reaction zones A and A' which contain one or more catalysts capable of catalyzing oxidation of propylene to acrolein, reaction zones B and B' which contain one or more catalysts capable of catalyzing

oxidation of acrolein to acrylic acid and a reaction zone C containing a high surface area material having heat transfer properties and 0 percent catalyst, disposed between reaction zones A' and B, wherein the reaction zones A and A' have a different catalytic activity for converting propylene to acrolein and reaction zones B and B' have a different catalytic activity for converting acrolein to acrylic acid, wherein the heat transfer zones are formed by at least one perforated tube sheet through which the catalytic contact tubes pass, and (B) contacting the reactant composition with the two or more reaction zones to form a mixed product gas comprising acrylic acid.

36. Use of a reactant composition in a process for vapor phase oxidation of propylene to acrylic acid in a single reactor, the composition consisting of:

- (i) 7.6 to 11 percent by volume propylene,
- (ii) oxygen in an amount suitable to provide an oxygen to propylene ratio of 1.6 to 2.2 : 1.0,
- (iii) 2 to 12 percent by volume water vapor, and
- (iv) the remainder comprising a major amount of at least one inert gas selected from the group consisting of nitrogen, helium, argon and mixtures thereof, and a minor amount of at least one inert gas fuel.

37. The use of claim 36, wherein the at least one inert gas is nitrogen.

38. The use reactant feed composition of claim 36, wherein the at least one inert gas fuel is propane.

#### Patentansprüche

1. Verfahren zur Dampfphasenoxidation von Propylen zu Acrylsäure, umfassend die Schritte:

(A) Zuführen einer Reaktionszusammensetzung umfassend:

- (i) mindestens 7,6 Volumenprozent Propylen,
- (ii) Sauerstoff,
- (iii) Wasserdampf, und
- (iv) den Rest umfassend eine größere Menge von Inertgas,

in einen Reaktor, wobei der Reaktor eine Vielzahl von Kontaktrohren aufweist, die mindestens einen Katalysator enthalten und in einer Hülle angeordnet sind, wobei das Innere der Reaktorhülle in mindestens erste und zweite Wärmeübertragungszonen geteilt ist, durch die jeweils ein Wärmeübertragungsmedium läuft und wobei jedes Kontaktrohr zwei oder mehr Reaktionszonen umfasst, die die Herstellung von Acrylsäure aus Propylen bewirken können, wobei die Wärmeübertragungszonen durch mindestens einen perforierten Rohrboden gebildet werden, durch den die katalytischen Kontaktrohre laufen; und

(B) Inkontaktbringen der Reaktionszusammensetzung mit den zwei oder mehr Reaktionszonen, um ein gemischtes Produktgas, umfassend Acrylsäure, zu bilden.

2. Das Verfahren nach Anspruch 1, wobei die Reaktionszusammensetzung 7,6 bis 11 Volumenprozent Propylen enthält.

3. Das Verfahren nach Anspruch 1, wobei in der Reaktionszusammensetzung Sauerstoff in einer Menge anwesend ist, die ein Sauerstoff/Propylen-Verhältnis von 1,6 zu 2,0 : 1,0 liefert.

4. Das Verfahren nach Anspruch 1, wobei die Reaktionszusammensetzung 2 bis 12 Volumenprozent Wasserdampf enthält.

5. Das Verfahren nach Anspruch 1, wobei die Wärmeübertragungszonen durch mindestens einen perforierten Rohrboden gebildet werden, durch den die katalytischen Kontaktrohre laufen.

6. Das Verfahren nach Anspruch 1, wobei die zwei oder mehr Reaktionszonen eine Reaktionszone A, enthaltend Katalysator, der mindestens die Oxidation von Propylen zu Acrolein katalysieren kann, und eine Reaktionszone B, enthaltend Katalysator, der mindestens die Oxidation von Acrolein zu Acrylsäure katalysieren kann, aufweist.

7. Das Verfahren nach Anspruch 6, wobei die zwei oder mehr Reaktionszonen überlappen können.
8. Das Verfahren nach Anspruch 6, wobei die Reaktionszonen A und B innerhalb der Reaktorrohre sequentiell angeordnet sind, so dass die Reaktionspartner zuerst mit der Reaktionszone A und dann mit der Reaktionszone B in Kontakt treten.
9. Das Verfahren nach Anspruch 9, wobei die zwei oder mehr Reaktionszonen Reaktionszonen A und A', die einen oder mehr Katalysatoren enthalten, die mindestens die Oxidation von Propylen zu Acrolein katalysieren können, und Reaktionszonen B und B', die einen oder mehr Katalysatoren enthalten, die mindestens die Oxidation von Acrolein zu Acrylsäure katalysieren können, aufweisen.
10. Das Verfahren nach Anspruch 9, wobei die Reaktionszonen A und A' eine unterschiedliche katalytische Aktivität hinsichtlich der Umwandlung von Propylen zu Acrolein aufweisen.
11. Das Verfahren nach Anspruch 10, wobei die Reaktionszonen B und B' eine unterschiedliche katalytische Aktivität im Hinblick auf die Umwandlung von Acrolein zu Acrylsäure aufweisen.
12. Das Verfahren nach Anspruch 6, wobei das Kontaktrohr weiter eine Reaktionszone umfasst, die 0 Prozent Katalysator, angeordnet zwischen den ersten und zweiten Reaktionszonen, enthält.
13. Das Verfahren nach Anspruch 9, wobei das Kontaktrohr weiter eine Reaktionszone umfasst, die 0 Prozent Katalysator, angeordnet zwischen den Reaktionszonen A' und B enthält.
14. Das Verfahren nach Anspruch 1, wobei der Reaktor mehr als 15.000 Kontaktrohre enthält.
15. Das Verfahren nach Anspruch 9, wobei die Verhältnisse von A'/A und B'/B beide 1,0:1 bis 3,0:1 betragen.
16. Das Verfahren nach Anspruch 1, wobei die erste Wärmeübertragungszone bei einer Temperatur von 250 bis 450°C gehalten wird.
17. Das Verfahren nach Anspruch 1, wobei die zweite Wärmeübertragungszone bei einer Temperatur von 220 bis 450°C gehalten wird.
18. Das Verfahren nach Anspruch 1, wobei das Wärmeübertragungsmedium innerhalb des Reaktors in gleicher Richtung mit dem Strom der Reaktionspartner zirkuliert.
19. Das Verfahren nach Anspruch 1, wobei das Wärmeübertragungsmedium innerhalb des Reaktors in entgegengesetzte Richtung zu dem Strom der Reaktionspartner zirkuliert.
20. Das Verfahren nach Anspruch 1, wobei das Wärmeübertragungsmedium innerhalb des Reaktors in mindestens zwei verschiedenen Wärmeübertragungsmediumkreisläufen zirkuliert.
21. Das Verfahren nach Anspruch 1, wobei das Wärmeübertragungsmedium in den Reaktor durch die Hülle an einer Vielzahl von Eintrittspunkten eintritt.
22. Das Verfahren nach Anspruch 18, wobei das Wärmeübertragungsmedium innerhalb des Reaktors sowohl in gleicher Richtung mit den Reaktionspartnern als auch transversal weg von der und hin zu der Mitte des Reaktors in einem schlängelnden Strom zirkuliert.
23. Das Verfahren nach Anspruch 20, wobei mindestens einer der Wärmeübertragungsmediumkreisläufe einen Kühlkreislauf enthält, wobei ein Teil des Wärmeübertragungsmediums des Wärmeübertragungsmediumkreisläufes zu dem Äußeren des Reaktors zwecks Kühlen zirkuliert und dann zu mindestens einem der Wärmeübertragungsmediumkreisläufe zurückgeführt wird.
24. Das Verfahren nach Anspruch 20, wobei das Wärmeübertragungsmedium innerhalb des Reaktors in mindestens zwei separaten Wärmeübertragungsmediumkreisläufen zirkuliert, von denen mindestens einer ein Bypass-Kreislauf ist, wobei mindestens ein Teil des Wärmeübertragungsmediums direkt zirkuliert, dass den Kontakt mit mindestens einem Teil der Kontaktrohre umgeht.

25. Das Verfahren nach Anspruch 1, weiter umfassend Schritt (C) des Inkontaktbringens des gemischten Produktgases mit einem wässrigen Strom in einem Trockenturm, um eine wässrige Acrylsäurelösung zu erhalten.

26. Das Verfahren nach Anspruch 25, wobei mindestens ein Teil des während Schritt (C) erzeugten Absorptionsgases mit Reaktionspartnern vereinigt wird, um die Reaktionszusammensetzung zu bilden.

27. Das Verfahren nach Anspruch 26, wobei der Teil des bereitgestellten Absorptionsgases eine geeignete Menge ist, um mindestens 7,6 Volumenprozent Propylen in der Reaktionszusammensetzung zu halten.

28. Das Verfahren nach Anspruch 25, wobei der wässrige Strom Wasser und mindestens einen Polymerisationsinhibitor umfasst.

29. Das Verfahren nach Anspruch 28, wobei der mindestens eine Polymerisationsinhibitor ausgewählt ist aus einem wasserlöslichen oder alkohollöslichen Polymerisationsinhibitor.

30. Das Verfahren nach Anspruch 28, wobei der mindestens eine Polymerisationsinhibitor in Kombination mit Sauerstoff eingesetzt wird.

31. Das Verfahren nach Anspruch 25, wobei der wässrige Strom weniger als 3,0 Gewichtsprozent Essigsäure umfasst.

32. Das Verfahren nach Anspruch 31, wobei mindestens ein Teil des wässrigen Stroms ein recycelter Abwasserstrom ist.

33. Das Verfahren nach Anspruch 25, weiter umfassend Schritt (D) des Abtreibens leichter Enden aus der wässrigen Acrylsäurelösung, die aus dem Absorptionsmittel ausströmt.

34. Verfahren zur Dampfphasenoxidation von Propylen zu Acrylsäure wie in Anspruch 1 beansprucht, umfassend die Schritte

(A) Zuführen einer Reaktionszusammensetzung umfassend:

(i) mindestens 7,6 Volumenprozent Propylen,

(ii) Sauerstoff,

(iii) Wasserdampf, und

(iv) den Rest umfassend eine größere Menge von Inertgas und eine kleinere Menge von mindestens einem Inertgas, das für den Einsatz als Treibstoff geeignet ist, in einen Reaktor, wobei der Reaktor eine Vielzahl von Kontaktrohren aufweist, die mindestens einen Katalysator enthalten und in einer Hülle angeordnet sind, wobei das Innere der Reaktorhülle in mindestens erste und zweite Wärmeübertragungszonen geteilt ist, durch die jeweils ein Wärmeübertragungsmedium läuft und wobei jedes Kontaktrohr zwei oder mehr Reaktionszonen umfasst, die die Herstellung von Acrylsäure aus Propylen bewirken können, wobei die Wärmeübertragungszonen durch mindestens einen perforierten Rohrboden gebildet werden, durch den die katalytischen Kontaktrohre laufen; und

(B) Inkontaktbringen der Reaktionszusammensetzung mit den zwei oder mehr Reaktionszonen, um ein gemischtes Produktgas, umfassend Acrylsäure, zu bilden.

35. Verfahren zur Dampfphasenoxidation von Propylen zu Acrylsäure wie in Anspruch 1 beansprucht, umfassend die Schritte

(A) Zuführen einer Reaktionszusammensetzung umfassend:

(i) mindestens 7,6 Volumenprozent Propylen,

(ii) Sauerstoff,

(iii) Wasserdampf, und

(iv) den Rest umfassend eine größere Menge von Inertgas

in einen Reaktor, wobei der Reaktor eine Vielzahl von Kontaktrohren aufweist, die mindestens einen Katalysator enthalten und in einer Hülle angeordnet sind, wobei das Innere der Hülle in erste und zweite Wärme-

übertragungszonen geteilt ist, durch die jeweils ein Wärmeübertragungsmedium in gleicher Richtung zu den Reaktionszusammensetzungsströmen läuft, wobei jedes Kontaktrohr mindestens umfasst Reaktionszonen A und A', die einen oder mehr Katalysatoren enthalten, die die Oxidation von Propylen zu Acrolein katalysieren können, Reaktionszonen B und B', die einen oder mehr Katalysatoren enthalten, die die Oxidation von Acrolein zu Acrylsäure katalysieren können, und eine Reaktionszone C, die ein Material mit hoher Oberfläche mit Wärmeübertragungseigenschaften und 0 Prozent Katalysator enthält, angeordnet zwischen Reaktionszonen A' und B, wobei die Reaktionszonen A und A' unterschiedliche katalytische Aktivität im Hinblick auf die Umwandlung von Propylen zu Acrolein und die Reaktionszonen B und B' unterschiedliche katalytische Aktivität im Hinblick auf die Umwandlung von Acrolein zu Acrylsäure aufweisen, wobei die Wärmeübertragungszonen durch mindestens einen perforierten Rohrboden gebildet werden, durch den die katalytischen Kontaktrohre laufen, und

(B) Inkontaktbringen der Reaktionszusammensetzung mit den zwei oder mehr Reaktionszonen, um ein gemischtes Produktgas, umfassend Acrylsäure, zu bilden.

36. Verwendung einer Reaktionszusammensetzung in einem Verfahren zur Dampfphasenoxidation von Propylen zu Acrylsäure in einem Einzelreaktor, die Zusammensetzung bestehend aus:

- (i) 7,6 Volumenprozent Propylen,
- (ii) Sauerstoff in einer Menge, die geeignet ist, um ein Verhältnis von Sauerstoff zu Propylen von 1,6 bis 2,2 : 1,0 zu ergeben,
- (iii) 2 bis 12 Volumenprozent Wasserdampf, und
- (iv) dem Rest, umfassend eine größere Menge von mindestens einem Inertgas, ausgewählt aus der Gruppe bestehend aus Stickstoff, Helium, Argon und Gemischen davon, und einer kleineren Menge von mindestens einem Inertgas-Treibstoff.

37. Die Verwendung gemäß Anspruch 36, wobei das mindestens eine Inertgas Stickstoff ist.

38. Die Verwendung gemäß Anspruch 36, wobei der mindestens eine Inertgas-Treibstoff Propan ist.

#### Revendications

1. Procédé d'oxydation en phase vapeur de propylène en acide acrylique, comprenant les étapes consistant à :

(A) charger dans un réacteur une composition de réactifs comprenant :

- (i) au moins 7,6 pour cent en volume de propylène,
- (ii) de l'oxygène,
- (iii) de la vapeur d'eau, et
- (iv) le restant comprenant une proportion majeure de gaz inerte;

le réacteur comprenant une pluralité de tubes de contact, contenant au moins un catalyseur, disposés dans une enveloppe, l'intérieur de l'enveloppe du réacteur étant divisé en au moins une première et une deuxième zones de transfert de chaleur à travers chacune desquelles passe un agent de transfert de chaleur, et chaque tube de contact comprenant deux ou plus de deux zones réactionnelles capables d'effectuer la préparation d'acide acrylique à partir de propylène, les zones de transfert de chaleur étant formées par au moins une plaque à tubes perforée traversée par les tubes de contact catalytiques; et

(B) mettre en contact la composition de réactifs avec les deux ou plus de deux zones réactionnelles pour former un mélange de produits gazeux comprenant de l'acide acrylique.

2. Procédé selon la revendication 1, dans lequel la composition de réactifs contient 7,6 à 11 pour cent en volume de propylène.

3. Procédé selon la revendication 1, dans lequel, dans la composition de réactifs, de l'oxygène est présent dans une proportion qui permet d'avoir un rapport oxygène/propylène de 1,6 à 2,0 pour 1,0.

4. Procédé selon la revendication 1, dans lequel la composition de réactifs contient 2 à 12 pour cent en volume de vapeur d'eau.



5. Procédé selon la revendication 1, dans lequel les zones de transfert de chaleur sont formées par au moins une plaque à tubes perforée traversée par les tubes de contact catalytiques.
- 5 6. Procédé selon la revendication 1, dans lequel les deux ou plus de deux zones réactionnelles comprennent une zone réactionnelle A contenant un catalyseur au moins capable de catalyser l'oxydation du propylène en acroléine et une zone réactionnelle B contenant un catalyseur au moins capable de catalyser l'oxydation de l'acroléine en acide acrylique.
7. Procédé selon la revendication 6, dans lequel les deux ou plus de deux zones réactionnelles peuvent se chevaucher.
- 10 8. Procédé selon la revendication 6, dans lequel les zones réactionnelles A et B sont placées successivement au sein des tubes du réacteur de telle sorte que les réactifs entrent en contact d'abord avec la zone réactionnelle A, puis avec la zone réactionnelle B.
- 15 9. Procédé selon la revendication 1, dans lequel les deux ou plus de deux zones réactionnelles comprennent des zones réactionnelles A et A' qui contiennent un ou plusieurs catalyseurs au moins capables de catalyser l'oxydation du propylène en acroléine et des zones réactionnelles B et B' qui contiennent un ou plusieurs catalyseurs au moins capables de catalyser l'oxydation de l'acroléine en acide acrylique.
- 20 10. Procédé selon la revendication 9, dans lequel les zones réactionnelles A et A' ont une activité catalytique différente pour transformer le propylène en acroléine.
- 25 11. Procédé selon la revendication 10, dans lequel les zones réactionnelles B et B' ont une activité catalytique différente pour transformer l'acroléine en acide acrylique.
12. Procédé selon la revendication 6, dans lequel le tube de contact comprend, en outre, une zone réactionnelle contenant 0 pour cent de catalyseur placée entre les première et deuxième zones réactionnelles.
- 30 13. Procédé selon la revendication 9, dans lequel le tube de contact comprend, en outre, une zone réactionnelle contenant 0 pour cent de catalyseur placée entre les zones réactionnelles A' et B.
14. Procédé selon la revendication 1, dans lequel le réacteur contient plus de 15 000 tubes de contact.
- 35 15. Procédé selon la revendication 9, dans lequel les rapports A'/A et B'/B ont tous deux des valeurs de 1,0:1 à 3,0:1.
16. Procédé selon la revendication 1, dans lequel la première zone de transfert de chaleur est maintenue à une température de 250 à 450°C.
- 40 17. Procédé selon la revendication 1, dans lequel la deuxième zone de transfert de chaleur est maintenue à une température de 220 à 450°C.
18. Procédé selon la revendication 1, dans lequel l'agent de transfert de chaleur circule au sein du réacteur à co-courant avec le flux des réactifs.
- 45 19. Procédé selon la revendication 1, dans lequel l'agent de transfert de chaleur circule au sein du réacteur à contre-courant avec le flux des réactifs.
20. Procédé selon la revendication 1, dans lequel l'agent de transfert de chaleur circule au sein du réacteur dans au moins deux circuits d'agent de transfert de chaleur distincts.
- 50 21. Procédé selon la revendication 1, dans lequel l'agent de transfert de chaleur pénètre dans le réacteur en traversant l'enveloppe par une pluralité de points d'entrée.
- 55 22. Procédé selon la revendication 18, dans lequel l'agent de transfert de chaleur circule au sein du réacteur à la fois à co-courant avec les réactifs et transversalement, à la fois en s'écartant et en se rapprochant du centre du réacteur selon un écoulement en méandres.

23. Procédé selon la revendication 20, dans lequel au moins un des circuits d'agent de transfert de chaleur contient un circuit de refroidissement grâce auquel une partie de l'agent de transfert de chaleur du circuit d'agent de transfert de chaleur est mise en circulation vers l'extérieur du réacteur pour refroidir, puis renvoyée vers au moins un des circuits d'agent de transfert de chaleur.

24. Procédé selon la revendication 20, dans lequel l'agent de transfert de chaleur circule au sein du réacteur dans au moins deux circuits d'agent de transfert de chaleur distincts, dont l'un au moins est un circuit de dérivation dans lequel au moins une partie de l'agent de transfert de chaleur circule de manière à éviter le contact avec au moins une partie des tubes de contact.

25. Procédé selon la revendication 1, comprenant en outre l'étape (C) qui consiste à mettre en contact le mélange de produits gazeux avec un courant aqueux dans une tour d'absorption pour obtenir une solution aqueuse d'acide acrylique.

26. Procédé selon la revendication 25, dans lequel au moins une partie des effluents gazeux de l'absorbeur produits au cours de l'étape (C) est combinée avec les réactifs pour former la composition de réactifs.

27. Procédé selon la revendication 26, dans lequel la partie des effluents gazeux de l'absorbeur fournie est une proportion appropriée pour maintenir dans la composition de réactifs au moins 7,6 pour cent en volume de propylène.

28. Procédé selon la revendication 25, dans lequel le courant aqueux comprend de l'eau et au moins un inhibiteur de polymérisation.

29. Procédé selon la revendication 28, dans lequel l'inhibiteur de polymérisation, au nombre d'au moins un, est choisi parmi un inhibiteur de polymérisation soluble dans l'eau et un inhibiteur de polymérisation soluble dans les alcools.

30. Procédé selon la revendication 28, dans lequel l'inhibiteur de polymérisation, au nombre d'au moins un, est utilisé en combinaison avec de l'oxygène.

31. Procédé selon la revendication 25, dans lequel le courant aqueux comprend moins de 3,0 pour cent en poids d'acide acétique.

32. Procédé selon la revendication 31, dans lequel au moins une partie du courant aqueux est un courant d'eaux résiduelles recyclé.

33. Procédé selon la revendication 25, comprenant en outre l'étape (D) consistant à distiller les fractions légères de la solution aqueuse d'acide acrylique émanant de l'absorbeur.

34. Procédé d'oxydation en phase vapeur de propylène en acide acrylique selon la revendication 1, comprenant les étapes consistant à :

(A) charger dans un réacteur une composition de réactifs comprenant :

(i) au moins 7,6 pour cent en volume de propylène,

(ii) de l'oxygène,

(iii) de la vapeur d'eau, et

(iv) le restant étant une proportion majeure d'au moins gaz inerte et une proportion mineure d'au moins un gaz inerte qui convient pour être utilisé comme combustible;

le réacteur comprenant une pluralité de tubes de contact contenant au moins un catalyseur, disposés dans une enveloppe, l'intérieur de l'enveloppe du réacteur étant divisé en une première et une deuxième zones de transfert de chaleur à travers chacune desquelles passe un agent de transfert de chaleur, chaque tube de contact comprenant deux ou plus de deux zones réactionnelles capables d'effectuer la préparation d'acide acrylique à partir de propylène, les zones de transfert de chaleur étant formées par au moins une plaque à tubes perforée traversée par les tubes de contact catalytiques; et

(B) mettre en contact la composition de réactifs avec les deux ou plus de deux zones réactionnelles pour former un mélange de produits gazeux comprenant de l'acide acrylique.

35. Procédé d'oxydation en phase vapeur de propylène en acide acrylique selon la revendication 1, comprenant les étapes consistant à :

(A) charger dans un réacteur une composition de réactifs comprenant :

- (i) au moins 7,6 pour cent en volume de propylène,
- (ii) de l'oxygène,
- (iii) de la vapeur d'eau, et
- (iv) le restant étant une proportion majeure d'au moins un gaz inerte;

le réacteur comprenant une pluralité de tubes de contact contenant au moins un catalyseur disposé dans une enveloppe, l'intérieur de l'enveloppe étant divisé en une première et une deuxième zones de transfert de chaleur à travers chacune desquelles passe un agent de transfert de chaleur à co-courant avec le flux de composition de réactifs, chaque tube de contact comprenant au moins des zones réactionnelles A et A' qui contiennent un ou plusieurs catalyseurs capables de catalyser l'oxydation du propylène en acroléine, des zones réactionnelles B et B' qui contiennent un ou plusieurs catalyseurs capables de catalyser l'oxydation de l'acroléine en acide acrylique et une zone réactionnelle C contenant un matériau de grande surface spécifique ayant des propriétés de transfert de chaleur et 0 pour cent de catalyseur, disposée entre les zones réactionnelles A' et B, où les zones réactionnelles A et A' ont une activité catalytique différente pour transformer le propylène en acroléine et les zones réactionnelles B et B' ont une activité catalytique différente pour transformer l'acroléine en acide acrylique, les zones de transfert de chaleur étant formées par au moins une plaque à tubes perforée traversée par les tubes de contact catalytiques; et

(B) mettre en contact la composition de réactifs avec les deux ou plus de deux zones réactionnelles pour former un mélange de produits gazeux comprenant de l'acide acrylique.

36. Utilisation d'une composition de réactifs dans un procédé d'oxydation en phase vapeur de propylène en acide acrylique dans un seul réacteur, la composition étant constituée :

- (i) de 7,6 à 11 pour cent en volume de propylène,
- (ii) d'oxygène dans une proportion qui permet d'avoir un rapport oxygène/propylène de 1,6 à 2,2 pour 1,0,
- (iii) de 2 à 12 pour cent en volume de vapeur d'eau, et
- (iv) le restant comprenant une proportion majeure d'au moins un gaz inerte choisi dans le groupe constitué par l'azote, l'hélium, l'argon, et leurs mélanges, et une proportion mineure d'au moins un gaz inerte combustible.

37. Utilisation selon la revendication 36, dans laquelle le gaz inerte, au nombre d'au moins un, est l'azote.

38. Utilisation d'une composition de charge de réactifs selon la revendication 36, dans laquelle le gaz inerte combustible, au nombre d'au moins un, est le propane.

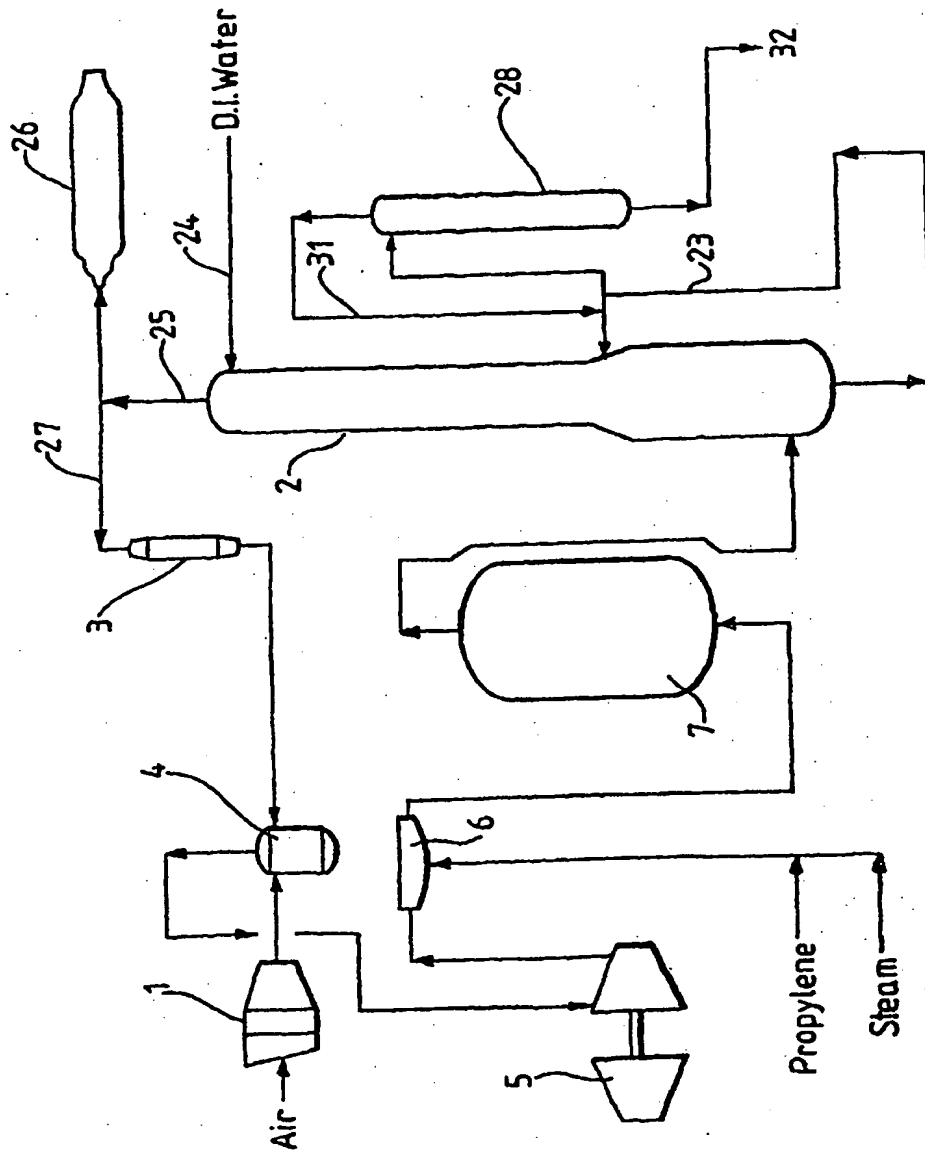


Fig.1.

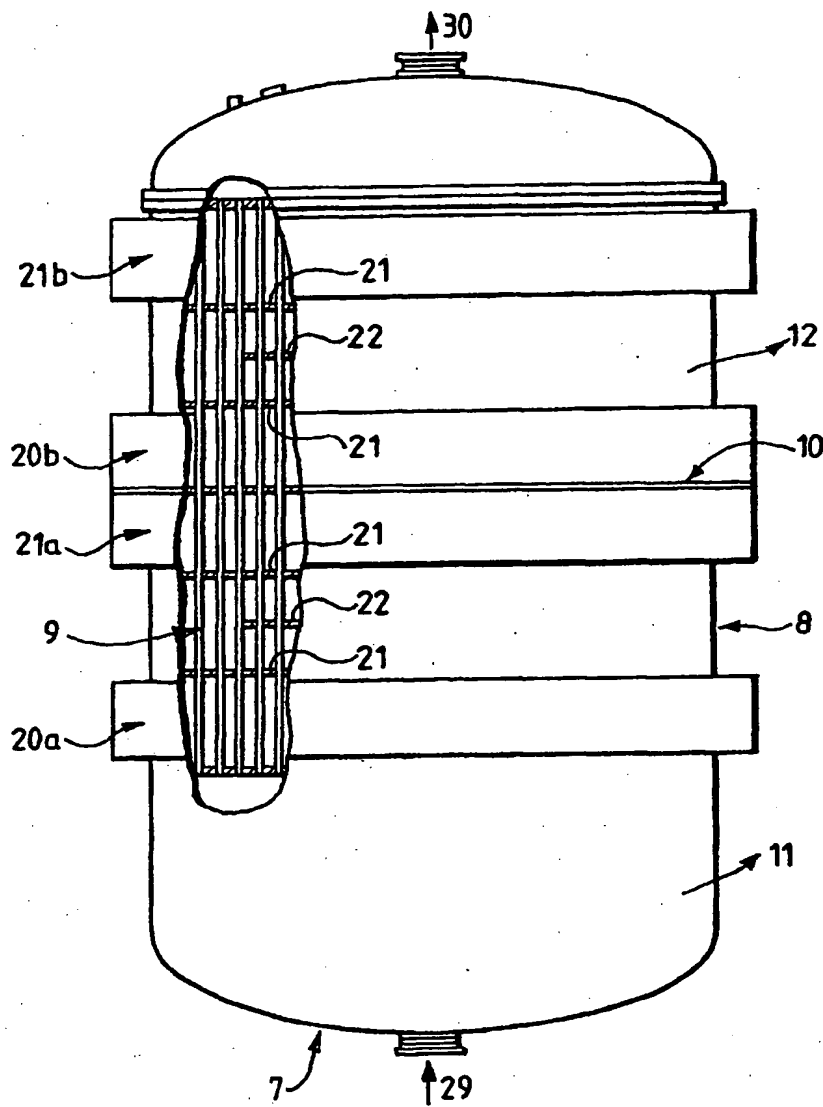


Fig. 2.

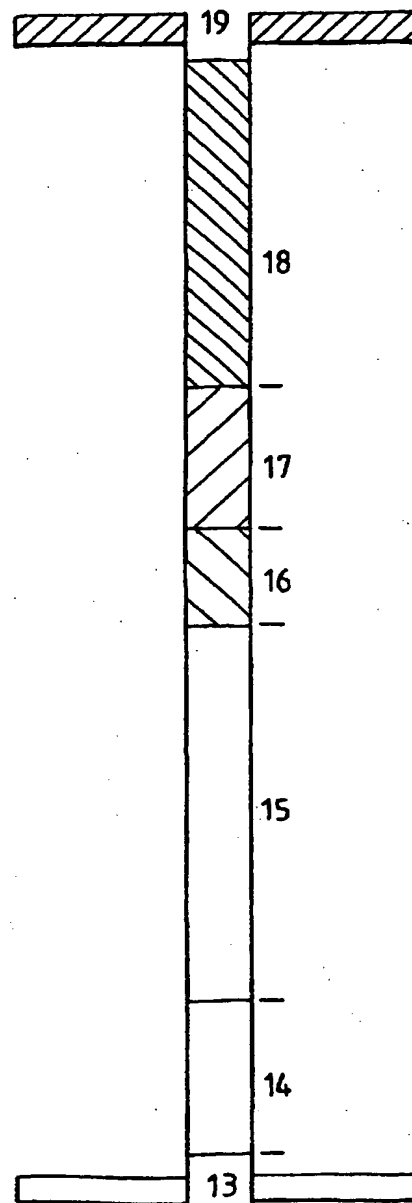


Fig.3.